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THE OUTLOOK FOR USING PALLADIUM AND 4th PERIOD METAL OXIDES IN HYDROGEN ENERGY AND TRANSPORT

GUSEV A. L., KUDEL’KINA E. V., CHABAN P. A., IVKIN A.V.

Russian Federal Nuclear Center – All-Russian Research Institute of Experimental Physics (RFNC-VNIIEF)

TURHAN NEDJAT VEZIROGLU
Clean Energy Research Institute University of Miami

MICHAEL DOUGLAS HAMPTON
University of Central Florida

1. INTRODUCTION

It is known that 50% of the world’s resources of palladium are found in Russia. This has opened avenues for revival of the Russian economy for development of hydrogen energy. In the present state of the art, hydrogen energy is based on liquid storage systems that requires further improvement of cryogenic facilities. In this connection is necessary to devise a great variety of low-temperature devices: sensors, chemical adsorbents, and zeolites that operate in the airless environment of heat-insulation vacuum cavities. To ensure normal operation of these systems at low temperatures one must employ catalysts and oxygen accumulators.

The objective of this work is the estimation of potential need for palladium in hydrogen energy and transport.

2. FIELDS OF APPLICATION

Systems to produce and purify hydrogen, low-temperature hydrogen sensors, low-temperature chemical hydrogen adsorbents, electrolyzers, zeolites to maintain the vacuum in heat-insulation cavities of cryogenic hydrogen containers, hydrogen energy systems for thermostatic control of various structures.

3. METHODS

Metal oxides are considered to be the most readily available and popular catalysts. G.K. Boreskov and V.V. Popovski having studied the catalytic activity of the 4th period metal oxides relative to the oxidation of hydrogen, arrange the oxides in the following series according to their specific catalytic activities [1].

$T = 300^0\ C : Co_3O_4 > CuO > MnO_2 > NiO > Fe_2O_3 > ZnO > Cr_2O_3 > V_2O_5 > TiO_2$

$T = 150^0\ C : Co_3O_4 > CuO > MnO_2 > NiO > Fe_2O_3 > Cr_2O_3 > V_2O_5 > ZnO > TiO_2$

The dissociation of H_2 molecules into atomic hydrogen, carried out by any method, i.e. hydrogen atomization in the gas phase or addition of palladium to cause dissociative chemisorption of molecular hydrogen to produce atomic hydrogen, significantly accelerates the oxidation process. The application of metal oxides in combination with palladium ensures a high catalytic effect, whereby the metal oxide being the oxygen source promotes chemical processes in vacuum heat-insulation cavities.

4. APPROACHES

Chemical reaction of metal oxides with hydrogen in a low-temperature region (77-220K) is observed on *palladium-plated manganese dioxide only*, and may be presented as follows: hydrogen activation takes place in the oxide cluster involving partially reduced palladium ions [2]:

$$Pd^0 \ldots Pd^+ - 0 - Mn^{4+};$$
$$H_2 \qquad 2H;$$
$$H^{\cdot} + Pd^+ \rightarrow Pd^0 + H^+ \ (H + e)$$

These these processes promote the reaction between hydrogen and manganese dioxide at low temperature. The resulting proton reacts with the oxide ions to form water, $H^+ + O^{2-} \rightarrow OH^-$; $H^+ + OH^- \rightarrow H_2O$.

At lower temperatures, the activation process of proton passage becomes less probable, and the main role may be played by a proton spillover through the oxide lattice. The reduction of Mn^{4+} ion occurs when the electron passes from Pd^0 : $Pd^0 + Mn^{4+} \rightarrow Pd^+ + Mn^{3+}$. The occurrence of this reaction is confirmed by the fact that it has not been possible to completely reduce the palladium oxide cluster to Pd^0 on the metal oxide surface of low oxygen-binding energy.

It is not excluded that the electron transfer in this stage is carried out according to the tunneling mechanism.

Table 1 Dependence of the kinetic parameters of an individual and a palladized MnO^2 upon the amount of oxygen removed from the surface (V.M. Belousov, L.V. Lyashenko, etc.)

Chemical absorber temperature	**Surface content of oxygen**	**MnO_2**	**Activation energy**	**Pd-MnO_2**	**Activation energy**
T, K	*X*, %	$K_{sp}\cdot10^5$, $s^{-1}\cdot m^{-2}$	E_{act}, kJ/mole	$K_{sp}\cdot10^5$, $s^{-1}\cdot m^{-2}$	E_{act}, kJ/mole
295.00	0.00	13.00	17.60	35.60	38.00
	0.40	3.60	27.30	36.20	25.60
	0.70	–	–	58.00	24.20
	1.90	2.20	–	60.00	25.00
	2.40	0.40	–	–	–
	3.30	0.10	–	61.70	25.00
	5.10	0.08	37.60	68.80	21.20
	10.00	0.04	41.80	72.20	24.00
	12.00	0.00	–	102.00	19.00
	23.40	0.00	–	138.00	19.20
	100.00	–	–	290.00	15.00
273.00	100.00	–	–	206.00	–
206.00	100.00	–	–	148.00	15.00
163.00	100.00	–	–	52.00	–
77.00	100.00	–	–	36.00	0.50

4. CONSTRUCTION AND INNOVATIONS

Fig. 1 and 2 are portions of the cryogenic pipe with an automatic tracing system [3]. Fig. 3 and 6 present general views of chemical inversor-cartridges. The temperature operating range is of 77 to 373K. Fig. 7-8 are general views of a hydrogen piezosensor. To fabricate these devices, palladium and metals of the platinum group are required.

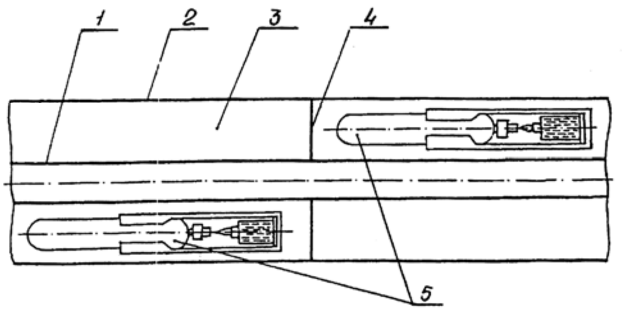

Figure1. 1 - cryogenic pipe; 2 – housing; 3 – vacuum section heat-insulation cavity; 4 – barrier that divides the heat-insulation vacuum space in the pipe into heat-insulation vacuum cavities; 5 – automatic tracing system case

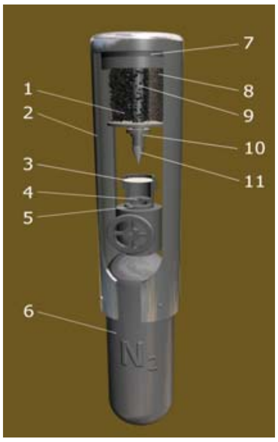

Figure 2. Automatic blast-proof system for hydrogen structures: 1 – thermochemical sensor; 2 – support; 3 – cylinder airtight plug; 4 – throttle; 5 – valve; 6 – cylinder with inert gas; 7 – washer; 8 – thermochemical sensor's punched walls; 9 – sensing material reacting with hydrogen and releasing heat; 10 – power cell with the form thermochemical storage; 11 – height-adjustable cutter

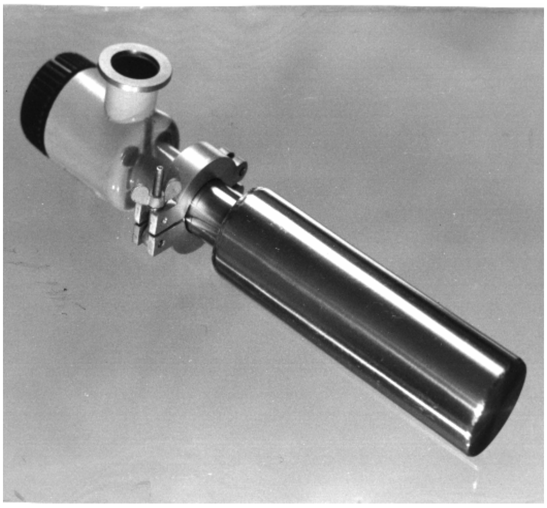

Figure 3. General view of chemical inversor-cartridge. Temperature operating range is of 77 to 373K

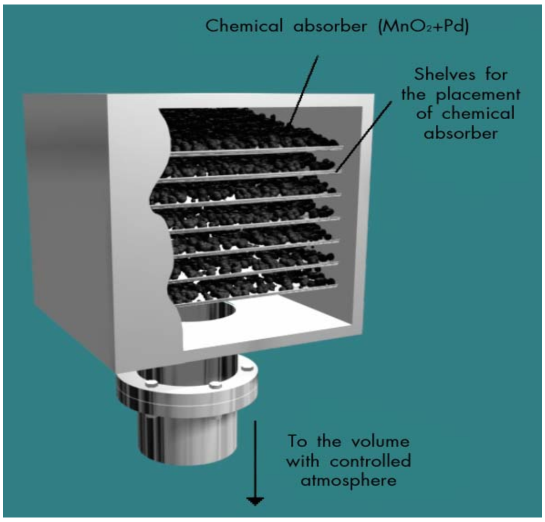

Figure 4. Chemical inversor-cartridge with shelves for uniform location of inverting material. Temperature operating

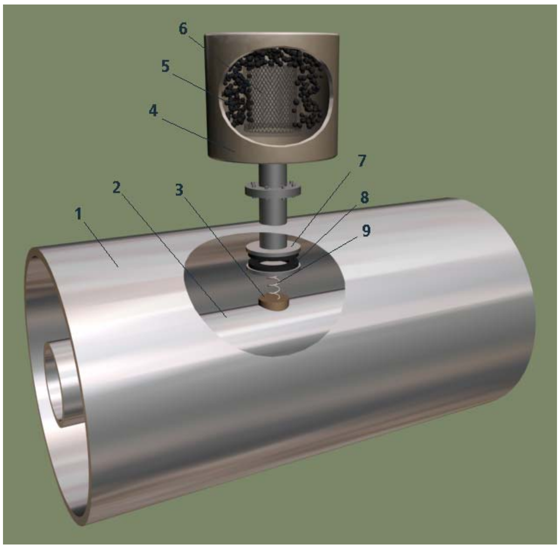

Figure 5. The cryogenic pipeline with a chemical cartridge

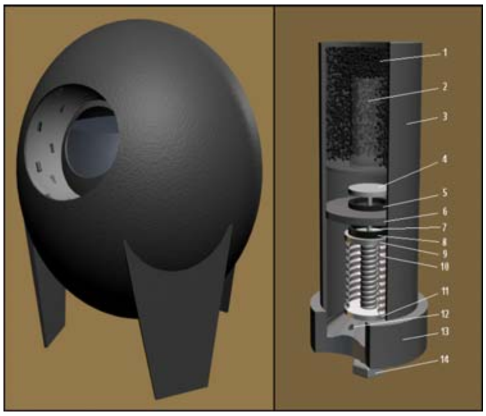

Figure 6. Accommodation of chemical cartridges in layers superinsulation of crygenicpump

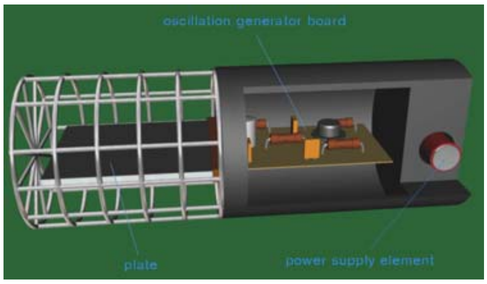

Figure 7. Hydrogen piezoresonance sensor: 1 – generator board; 2 – plate; 3 – power cell

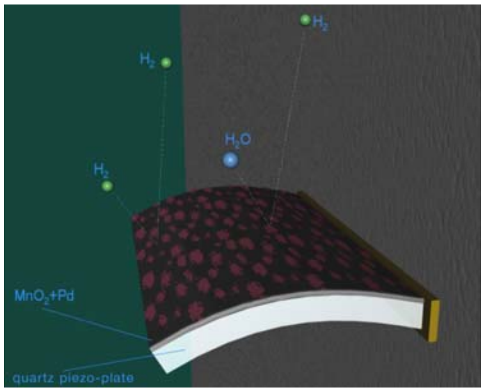

Figure 8. Sensor-coated quartz piezo plate

Figures 9 is general views of a thermochemical sensor control

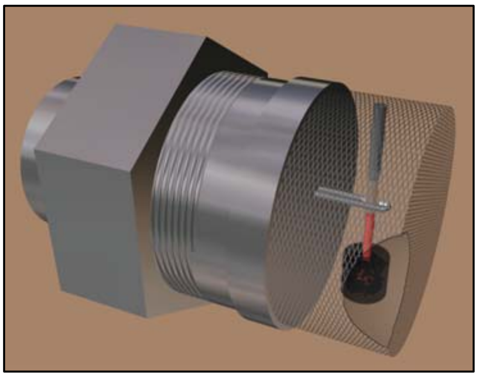

Figure 9. Thermochemical sensor control c optical input

CONCLUSION

It is known that 50% of the world's resources of palladium are found in Russia, thus ideally positioning Russia for the development of hydrogen energy. To date, with funding from ISTC Project #1580, a great deal of progress has been made on the creation of effective low temperature hydrogen sensors, chemical absorbents, and blast-proof systems. This work will contribute significantly to the development of hydrogen energy in Russia.

ACKNOWLEDGEMENTS

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[2]. V.M. Belousov, L.V.Lyashenko, I.V.Bacherikova, E.V. Rozhkova, - Kinetic principles of low-temperature interaction of individual and palladium-promoted manganese dioxide with hydrogen.- UCJ, 1994, vol. 60, No. 9, p. 627-630.

[3]. RU Patent No.2 103598. Cryogenic pipeline. – Gusev A.L., Kudryavtsev I.I., Turundaev A.P. Int. Cl. F 17D 5/00, F 16L 59/06. 1998.